EXPLORATORY STUDY ON PERVAPORATION MEMBRANES FOR REMOVAL OF WATER FROM WATER-CRUDE OIL EMULSIONS

FINAL REPORT

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1.0 INTRODUCTION

The prime objective of this study was to explore the feasibility of removeling water from oil/water (O/W) and water/oil (W/O) emulsions by means of pervaporation.

A review of literature and present technology suggested that there is considerable potential for membrane application to the separation of mixed liquids. Pervaporation has been used successfully in dehydration of multi-component mixed solvent systems such as methanol/water and ethanol/toluene/water mixtures.

Initial study involved preparation of simulated O/W and W/O emulsions prepared by mixing water and kerosene of various concentration and stablized by adding sodium lauryl sulfate.

Preliminery experiments were conducted on 12 membranes fabricated from two different materials. One membrane of each type of material was chosen for further work based on the results of preliminary tests.

During the preliminery tests, two different kinds of membranes, cellulose and polyvinylalcohol were used. The membranes were fabricated with or without supports. All experiments were carried out under two different down-stream pressures and various temperatures. These tests showed clearly that permeation rate increase at increasing temperatures. All membranes consistently permeated virtually pure water from the

feed.

High recovery (to a 90% volume reduction) experiments and a long run of 90%-oil emulsion test demonstrated that permeation rates could be rather high (4-6 grams per hour) when the oil content was less than 50%. The flux was then gradually reduced as the oil content increased to 70% and maintain with a low permeation rate. Hence, the operating configuration of the membrane system should be modified to improve the process.

Similarly, the flux remained low for the field emulsion experiments owing to the fact the viscosity of the crude oil samples was too high. Again, the process could be improved by a continuous-flow configuration and operating at a higher temperature.

As a result of this study, pervaporation has been evaluated for the removal of contaminating water from the heavy crude oil. The overall results reported has demonstrated the fact that over 97% of water has been recovered from a 10% kerosene-90% water emulsion by means of pervaporation while the oil separation was above 99% in most pervaporation experiments when the oil content varied from 10% to 90%. On the other hand, the product rate depended on the operating conditions, feed concentrations, and the membranes used. However, the dehydration of the crude oil sample was not efficient because of the high viscosity of the crude oil.

Further work should focus on developing membranes of higher performance; on assessing operation of configured membrane

systems for potential permeation rates; and larger pilot plant scale systems.

2.0 EXPERIMENTAL PROCEDURES

2.1 Membrane Fabrication

Polyvinylalcohol (PVA) membranes of various porosities have been prepared. Briefly, PVA polymer was first dissolved in a mixture of solvents (e.g. water and DMSO). The polymer solution was then filtered and degased. The solution was then cast onto a glass plate or various porous fabrics as supporting materials at various casting temperatures and periods of time and gelled by different gelation medium. Further crosslinking can be carried out treating the membrane with various crosslinking agents.

Cellulose pervaporation membranes have also been fabricated by similar method. A typical example can be illustrated by the following example: the membrane casting solution was prepared by mixing 26.3 g of methyl cellulose; 25.88 g of paraformaldehyde; and 0.14 g of potassium hydroxide in 243.4 g of DMSO. The solution was then well mixed at 125 degree C. for about two hours. After the solution was cooled down to 60°C, 12.94 g. of paraformaldehyde was further added and the temperature was raised to 125°C. for another hour. The solution was then cast at 122°C. with evaporation time of 10 min. and relative humidity of 30% and then was gelled in either water or ether.

Although both PVA and CE pervaporation membranes have been successfully used for the removal of contaminating water from the synthetic heavy crude oil, the stability and productivity of the membranes still demand further improvement. Obviously, membranes for pervaporation operated at elevated temperatures (80 °C. or

above) would upgrade the process.

2.2 Emulsion Preparation

Oil and water (O/W) emulsions were prepared by mixing various concentrations of kerosene and water together in the presence of (0.5 % by weight) sodium lauryl sulfate as surfactants. All the emulsions were well stirred and observed to be stable for at least over 48 hours. The kerosene contents in the emulsions varied from 10% to 90% while the content of the surfactant was kept constant. On the other hand, the field oil emulsions tested were obtained directly from the well head, Saskatcheween Oil Company.

2.3 Pervaporation Experiments

The pervaporation experiments were done for W/O and O/W emulsions with various oil concentration, namely from 10 to 90% in which surfactant was added to stablize the emulsions. All experiments were performed in a batch pervaporation cell of 250 ml capacity and with a membrane area of 9.6 sq. cm. An electro-magnetic bar was used to stir the solution. Experiments were carried out under two different pressure, namely 2-3 mm Hg and 10-12 mm Hg, and the operating temperature was varied from room temperature (23 $^{\circ}$C) to 78 $^{\circ}$C. The permeation rate was measured gravimetrically by an electronic balance. A flow diagram of the apparatus used was shown in Figure I.

2.4 Analytical Procedures

Conductivity

The conductivity was determined using a Extech conductivity meter Model 640 following the method described in the operating manual.

Total Organic Carbon (TOC)

The TOC was determined using a Beckman Model 915 TOC analyzer (Beckman Instrumenmts, Inc.) following the recommended procedure.

3.0 RESULTS AND DISCUSSION

3.1 Separation of W/O and O/W Emulsions by Pervaporation.

Polyvinylalcohol (PVA) and cellulose (CE) membranes of various porosities were fabricated. The membranes were first characterized by reverse osmosis experiments for reference solute separation (such as sodium chloride). The pure water and salt water tests yield information on the membrane performance. The membranes were then subjected to solvent exchange by treating with alcohol and hydrocarbon mixtures. The membranes remained stable after solvent treatment.

PVA membrane #11 was used for the oil emulsion separation. Pervaporation experiments were carried out with W/O and O/W emulsions with various oil concentration, namely from 10 to 90 % in which surfactant was added to stablize the emulsions. All PVA membranes tested exhibited very good TOC rejections of 99.8% or above. The permeates of all the experiments contained less than 0.2% oil as shown in Table I. Similar results were also obtained with cellulose membranes as shown in Table II.

The permeation rate of the pervaporation experiments varied with different operating conditions such as operating pressure in the downstream side, operating temperature and membranes used. The average permeation rate was about 4-6 grams per hour when the oil content is below 70% and decreased as the oil content increased. The permeation rate also increased with increase in temperature; it was, however, independent of downstream-side

pressure.

3.2 Effect of Temperature

Pervaporation experiments for the removal of water from oil emulsions were carried out at various operating temperatures by means of cellulose membranes. The experimental results were summarized in table 3-5 and illustrated in figure 2. Under the operating conditions chosen, the permeation rates increased by about 50% and 100% when the temperature was raised from the room temperature (25 °C) to 45 °C and 78 °C respectively as shown in table 6.

3.3 Effect of Membrane Material

Table 1-2 and Figure 3 showed the difference of membrane performance of PVA and CE. Although both membrane types exhibited very good TOC rejection, the permeation rate of PVA showed a higher productivity particularly when the oil content was higher than 20%. Furthermore, PVA membranes have also proved they were more thermally and chemically stable.

3.4 Effect of Oil Content

During the high recovery pervaporation experiments, the oil content of the synthetic oil emulsion was concentracted from 10 % to about 90% as shown in table 3 - 5 and figure 2. When the oil content was low, the permeation rates of the membrane were about 4-8 grams per hour. However, the permeation rates were reduced to less than one gram per hour as the oil content

was concentrated above 70%. It has been speculated that when the oil content was lower than 40%, the water was in continuous phase; and thus water permeation rate was high. On the other hand, when the oil content was above 70%, the continuous phase was no longer water, but oil. Therefore, the water permeation rate was reduced to less than one gram per hour.

3.5 Effect of Crude Oil

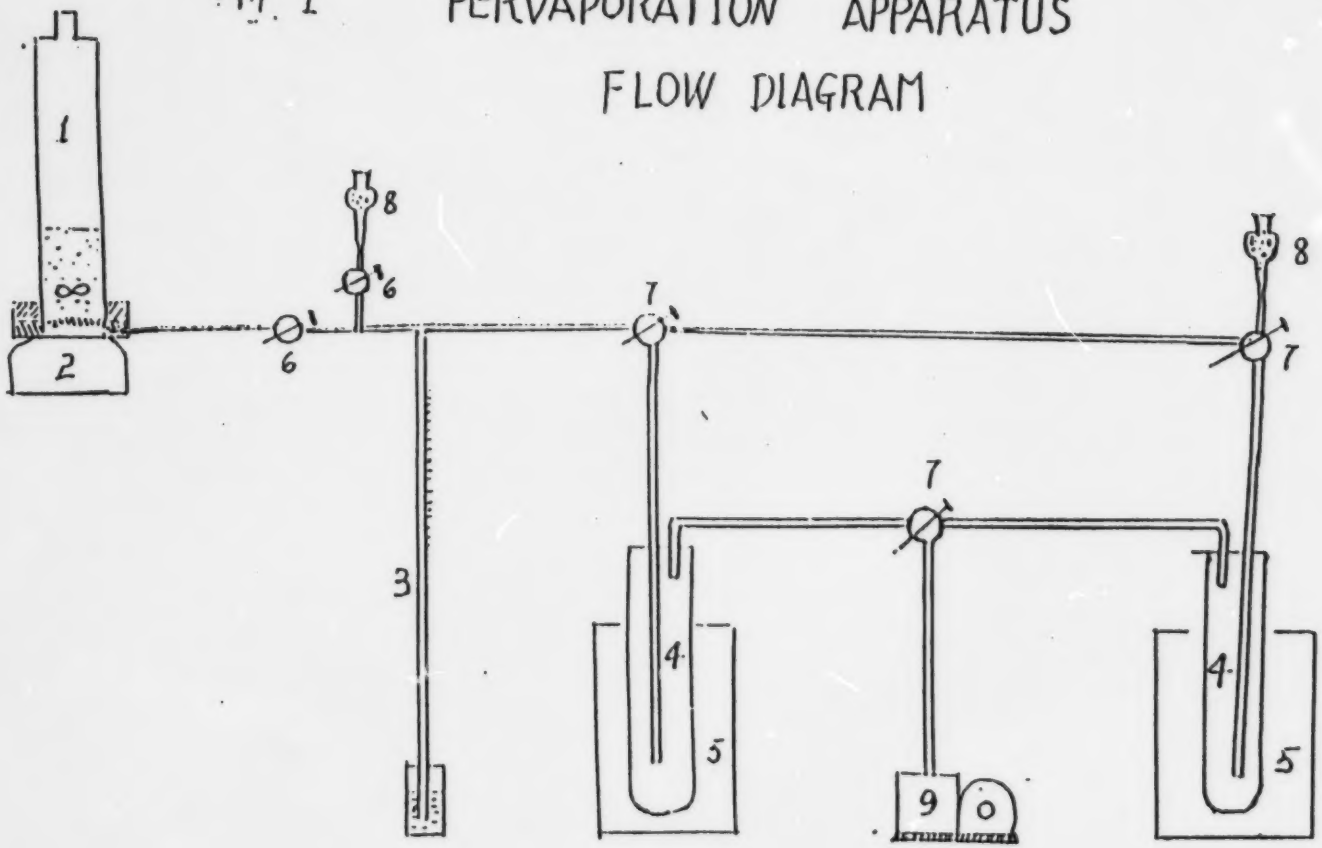
Although the permeation rate for the field oil emulsion was rather low as shown in table 7 and 8, oil rejection was still acceptable despite the fact that the membrane fouling was observed: the membrane performance with respect to the separation data for the reference solute, sodium chloride. Thus, further work focusing on developing membranes of higher performance (higher production rate and chemical and thermal stabililty) would facilitate the removal of water from the field oil emulsions.

4.0 CONCLUSIONS AND RECOMMENDATION

As a result of the exploratory studies examining the application of pervaporation to the removal of water from the oil emulsions, it has been successfully demonstrated that over 97% of water can be recovered from synthetic oil emulsions. The results has also proved that both cellulose and polyvinylalcohol membranes produced permeates relatively free of oil even when the synthetic or curde oil emulsions had oil content higher than 90%. Although cellulose membranes provided better product rate at low oil content, polyvinylalcohol had less fouling effect and thus exhibited high performance when oil content was higher than 20% and when the prevaporation was carried out at higher operating temperature. The study concluded that pervaporation was effective, but that more extensive studies on various field oil emulsions with improved membrane material and systems were necessary due to the complex and site specific characteristics of the actual field emulsions.

Fig. 1 PERVAPORATION APPARATUS

FLOW DIAGRAM



1. Cell for feed mixture
2. Electromagnetic stirrer
3 Mercury barometer
4 Permeate collector
5. Thermos with liquid nitrogen
6 Two-way valve
7 Three-way valve
8 Drier tube
9 Vacuum pump

Fig. 2 FLUX VERSUS CONCENTRATION AND TEMPERATURE

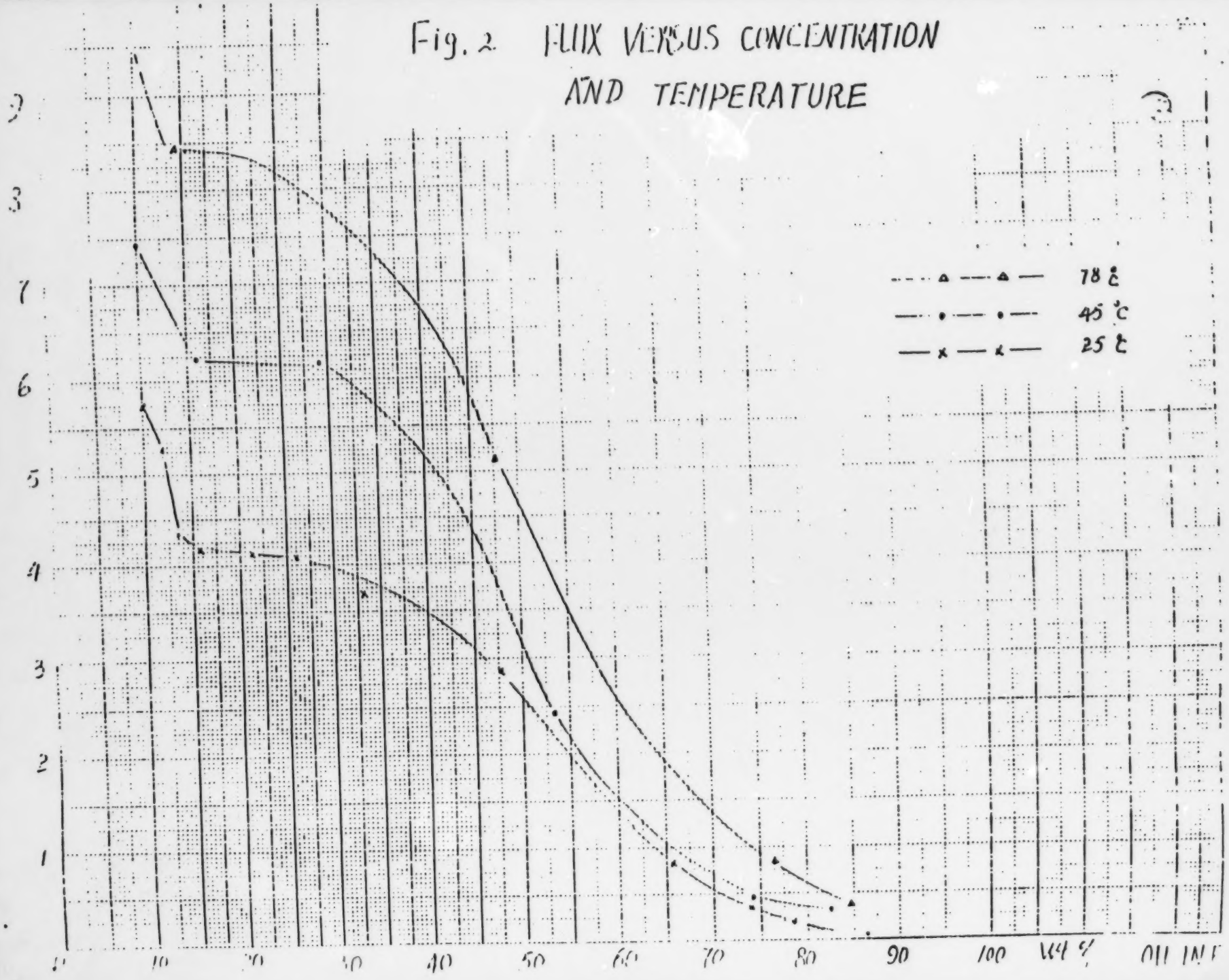


Fig. 3 FLUX VERSUS CONCENTRATION AND MEMBRANE TYPE

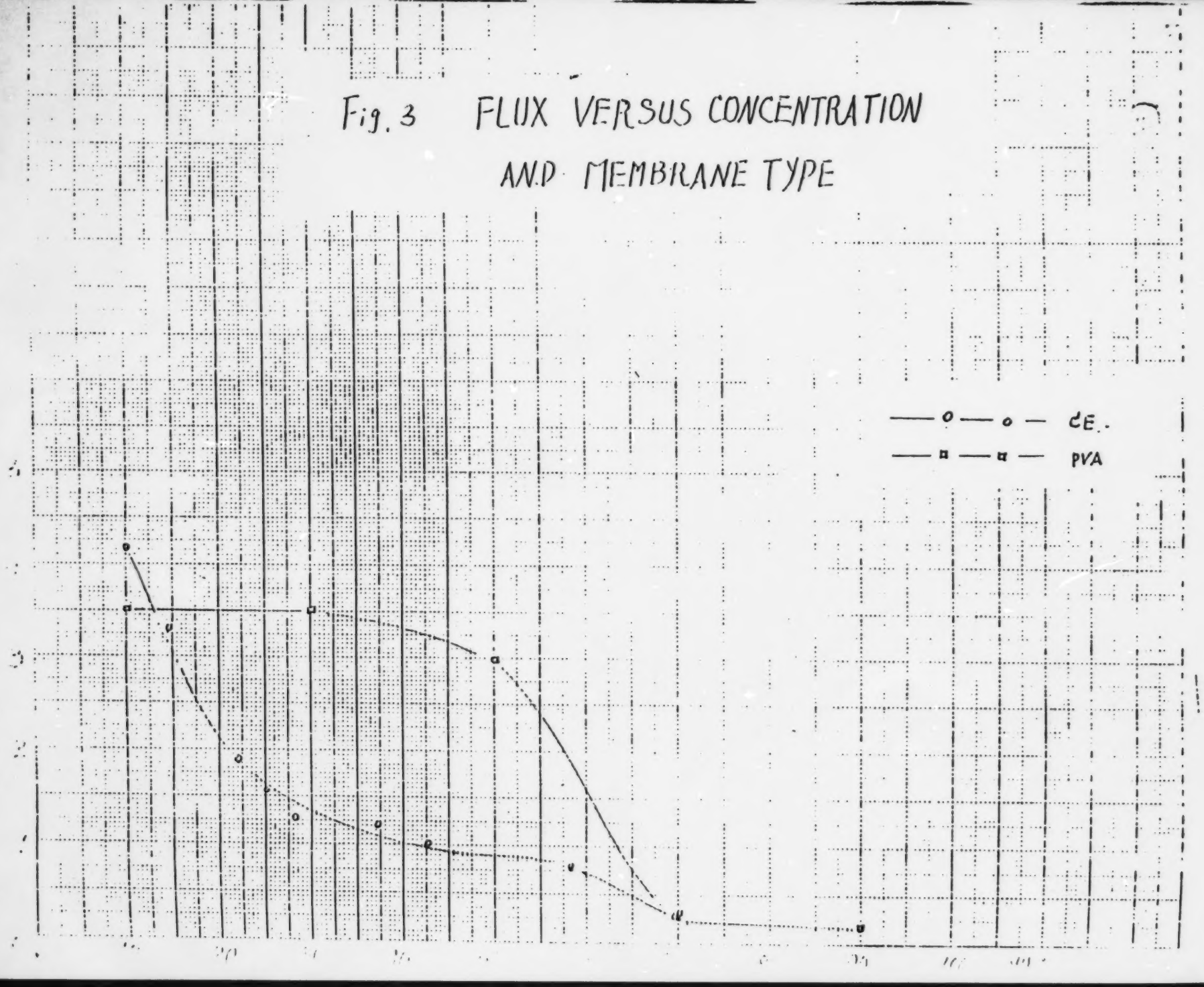


TABLE I

Emulsion Concentration %	Feed Components Total g	Water g	Permeate Total g	Separation (R) %	(PR) g/h	Oil Conc. in Residue %
10	135.0	122.0	24.73	99.8	3.53	12.24
30	136.6	95.62	22.05	99.83	3.58	35.77
50	110.2	55.12	24.50	99.98	2.98	64.29
70	122.0	36.60	5.50	99.97	0.29	73.31
90	107.7	10.77	3.24	99.95	0.19	92.79

PERVAPORATION OF OIL EMULSION BY PVA MEMBRANE

Membrane: membrane #11
Operating Temp. 24-25 C
Vacuum Pressure 10-12 mmHg

TABLE 2

Emulsion Concentration %	Feed Components Total g	Water g	Permeate Total g	Separation (R) %	(PR) g/h	Oil Conc. in Residue %
10	100.0	90.00	6.90	98.9	5.75	
30	30.27	20.27	9.30	99.93	3.72	
50	20.96	10.96	5.77	99.91	2.88	
70	13.45	3.45	0.70	99.86	0.35	

PERVAPORATION OF OIL EMULSION BY CE MEMBRANE

Membrane: membrane #1
Operating Temp. 24-25 C
Vacuum Pressure 10-12 mmHg

THE RESULTS FOR LONG RUN OF OIL IN EMULSION AT 25 °C

Feed: Kerosene (10%) - Water (90%) Emulsion
Membrane: Cellulose (Sample No. 4 from Dr. Matsuura)

Table 3

Expt. No.	Operative time hours		Feed			Permeate			Recovery of Water	
	Duration hours	Cumulative hours	Total grams	Water grams	Oil %	Quantity grams	Flux g/h	Oil sepn. %	Cumulative grams	% original of feed
1	0.2	0.2	100.0000	90.0000	10.00	2.3013*	-	-		
2	1.2	1.4	100.0000	90.0000	10.00	6.9040	5.7530	98.90	6.9040	7.67**
3	2.0	3.4	93.0960	83.0960	10.74	10.1701	5.0850	99.60	17.0741	18.97
4	2.0	5.4	82.9259	72.9259	12.06	10.6573	5.3287	99.75	27.7314	30.81
5	2.0	7.4	72.2682	62.2686	13.84	8.7184	4.3592	99.81	36.4498	40.50
6	2.0	9.4	63.5502	53.5502	15.74	8.3670	4.1835	99.82	44.8168	49.80
7	2.0	11.4	55.1832	45.1832	18.12	8.4080	4.2040	99.86	53.2248	59.14
8	2.0	13.4	46.7752	36.7752	21.38	8.3000	4.1500	99.89	61.5248	68.36
9	2.0	15.4	38.4752	28.4752	25.99	8.2035	4.1018	99.91	69.7283	77.48
10	2.5	17.9	30.2717	20.2717	33.03	9.3068	3.7230	99.93	79.0351	87.82
11	2.0	19.9	20.9649	10.9649	47.70	5.7680	2.8840	99.91	84.8031	94.23
12	2.0	21.9	15.1969	5.1969	65.80	1.7460	0.8730	99.86	86.5491	96.17
13	2.0	23.9	13.4509	3.4509	74.34	0.7030	0.3515	99.86	87.2521	96.95
14	2.0	25.9	12.7479	2.7479	78.44	0.4060	0.2030	99.94	87.6581	97.40
	Residue		12.3419	2.3419	81.02					

*May include some residual water in the porous plate in the cell.
**Based on original water in the feed.
Operating Conditions: Effective membrane area: 9.6cm^2; operating temperature 24-25°C; vacuum pressure on permeate side: 10-12 mmHg; surfactant in emulsion: Sodium lauryl sulfate, 0.5 wt %; kerosene oil from Fisher Scientific.

Table 4 THE RESULTS FOR LONG RUN OF 10% OIL IN EMULSION AT 45 °C

No	period (hr)	total operating time (hr)	feed condition: oil amount (g)	feed condition: water amount (g)	feed condition: total amount (g)	feed condition: emulsion concentration oil %	permeat results: amount (g)	permeat results: flux (g/hr)	permeat results: oil separation (%)	water recovery: amount (g)	water recovery: rate %
25	0.50	0.5	12.4434	111.9901	124.4335	10.00	6.8550	—	—		
26	2.0	2.5	12.4434	111.9901	124.4335	10.00	14.9360	7.4680	99.04	14.9360	13.34
27	3.0	5.5	12.4434	97.0541	109.4975	11.36	18.8731	6.2921	99.17	33.8141	30.19
28	2.05	7.55	12.4434	78.1760	90.6194	13.73	12.5913	6.1421	99.47	46.4054	41.44
29	2.67	10.22	12.4434	65.5847	78.0281	15.95	16.6025	6.2259	99.77	63.0079	56.26
30*	3.0	13.22	12.4434	48.9822	61.4256	20.26	18.9970	6.3323	99.84	82.0049	73.23
31	3.08	16.30	12.4434	29.9852	42.4286	29.33	19.0610	6.1819	99.79	101.0659	90.25
32	2.72	19.02	12.4434	10.9242	23.3676	53.25	6.6065	2.4318	99.91	107.6724	96.14
33	3.5	22.52	12.4434	4.3177	16.7611	74.24	1.6697	0.4771	99.89	109.3421	97.64
34*	2.0	24.52	12.4434	2.6430	15.0914	82.45 84	0.6730	0.3365	99.65	110.0151	98.24
35	5.0	29.52	12.4434	1.9750	14.4184	86.30	0.2980	0.0596	—	110.3131	98.50
residue			12.4434	1.6770	14.1204	88.12					

The inside temperature of the cell: 44.0~45.6 °C

The Bath temperature: 49.5 °C

Membrane: Cellulose 7"

Vacuum pressure: 12-15 mmHg

* The emulsion in cell was kept stirring for midnight without perraporation process.

Table 5 THE RESULTS FOR LONG RUN OF 10% OIL IN EMULSION AT 78 °C

NO	period (hr)	total operating time (hr)	feed condition: oil amount (g)	feed condition: water amount (g)	feed condition: total amount (g)	feed condition: emulsion concentration (wt%)	permeat results: amount (g)	permeat results: flux (g/hr)	permeat results: oil separation (%)	water recovery: amount (g)	water recovery: rate (%)	
41	0.2	0.2	13.1023	117.9207	131.0230	10.00	5.5275	—	—			
42	2.0	2.2	13.1023	117.9207	131.0230	10.00	12.2880	6.1440	97.47	12.2880	10.42	
43	2.0	4.2	13.1023	105.6327	118.7350	11.03	13.7979	6.3990	98.95	25.0859	21.27	
44	2.0	6.2	13.1023	92.8348	105.9371	12.37	14.3765	7.1883	99.23	39.4624	33.47	
45	2.0	8.2	13.1023	78.4583	91.5606	14.31	16.9228	8.4614	99.35	56.3852	47.82	
46	1.97	10.11	13.1023	61.5355	74.6378	17.55	17.2090	8.7355	98.97	73.5942	62.41	62.41
47*	2.0	12.17	13.1023	44.3265	57.4288	22.81	14.0918	7.0459	98.61	92.6860	78.60	
48**	2.03	14.2	13.1023	25.2347	38.3370	34.18	10.8580	5.3488	99.61	103.5440	87.81	
49	2.0	16.2	13.1023	14.3767	27.4790	47.68	10.3285	5.1643	99.76	113.8725	96.57	
50	2.0	18.2	13.1023	4.0482	17.1505	76.40	1.6865	0.8433	99.75	115.5590	98.00	
51	3.77	21.97	13.1023	2.3617	15.4640	84.73	1.4160	0.3756	98.54	116.9750	99.20	
residue			13.1023	0.9057	14.0080	93.27						

the inside temperature of the cell: 77~78 °C

The Back temperature: 80.7 °C

Membrane: Cellulose 9#

Vacuum pressure: 25~35 mm Hg

* the emulsion in cell was kept stirring overnight without pervaporation.

** The tube was blocked for half an hour because of ice

TABLE 6

Membrane Performance at Various Temperatures

Oil %	25 C PR g/h	25 C f %	45 C PR g/h	45 C f %	78 C PR g/h	78 C f %
10	5.75	98.9	7.47	99.0	6.14	97.5
20	4.15	99.9	6.33	99.8	9.55	98.6
30	3.72	99.9	6.18	99.8	5.35	99.6
50	2.38	99.9			5.16	99.8
75	0.35	99.9	0.48	99.9	0.34	99.8

PERVAPORATION OF OIL EMULSION BY CE MEMBRANE

Membrane:	membrane #1
Operating Temp.	24-25 C
Vacuum Pressure	10-12 mmHg

THE RESULTS OF PERVAPORATION FOR THE SECOND CRUDE OIL SAMPLE

Table 7

expt NO.	Temp. (°C)	operation time (hr)	permeate quantity (grams)	Average flux (g/hr)	Average carbon content in permeate (ppm)
108~111	24°	10.5 *	0.1695	0.0226	1581
112~115	40	12.5	0.4022	0.0322	2565
116~118	60	18	0.6427	0.0357	4153

Membrane: 15# polyvinyl alcohol

Membrane properties: PWP = 15.2779 (400psig)

PR = 13.1548 (g/hr)

sep = 23.5 % (NaCl 35000ppm)

Feed: the second crude oil sample from: wellhead, Sask oil company (black, fluid)

Vacuum pressure: 12-15 mmHg

* 10.5 hours includes 3 hours for the preliminary operation.

THE RESULTS OF PERVAPORATION FOR THE FIRST CRUDE OIL SAMPLE

Table 8

exp. NO.	operative time		permeate		
	duration (hr)	cumulative (hr)	quantity (grams)	Flux (g/hr)	carbon content (ppm)
100	0.33	0.33	2.9540	—	—
101	7.5	7.83	0.1574	0.0210	379
102	9.0	16.83	0.1570	0.0195	875
103	13.5	30.33	0.1863	0.0138	893
104	9.5	39.83	0.1310	0.0138	1257
105	11.5	51.33	0.1330	0.0116	1455
106	7.0	58.33	0.0440	0.0063	—
107	10.5	68.83	0.0550	0.0052	—
total water abstracted 0.8637 (g)					

membrane: 14". cellulose with backing material

membrane properties: PWP = 15.5901 (g/hr) (500 psig)

PR = 13.3783 (g/hr)

sep = 8.5% (NaCl 3500 ppm)

feed: the first crude oil sample

(black.. very viscous. it is almost unfluid.)

Temperature: The bath temp. 80 °C

The inside temp. of the cell. 60 – 65 °C

Vacuum pressure: 12 – 15 mmHg